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(19)(CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for Producing a Sintered Dental Prosthesis

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Canada■✦■

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ABSTRACT OF THE DISCLOSURE

A dental prosthesis having very high density values, that is
sintered from noble metal powder mixtures having a bimodal or
5   multimodal particle size distribution is obtained when the drying
and sintering processes are carried out in a specific manner.
For this purpose the dried dental prosthesis produced from a slip
is subjected to a thermal treatment for 5 to 45 minutes at
temperatures of between 100 and 400°C, whereupon it is heated to
10   800°C at an average temperature increase of 50 to 300 k per
minute and heated to the sintering temperatures with increases of
20 to 200 K per minute. The sintering temperature lies between
$(T_{solidus}-200)$ and $(T_{solidus}-70)$, $T_{solidus}$ being the solidus
temperature of the sintered alloy. The cooling process must be
15   carried out under vacuum or under a protective gas.

The present invention relates to a process for producing a
sintered dental prosthesis having a structural matrix of a noble
metal powder mixture or of a noble metal alloy powder mixture
having a bimodal or multimodal particle size distribution an a
5   predominantly spherical shape. This mixture is stirred with a
mixing fluid consisting substantially of water so as to obtain a
slip capable of being moulded and compressible by expelling the
mixing fluid. The prosthesis is moulded from said slip on a
model of the teeth to be supported, applying the technology used
10   in dental ceramics, said model serving as burner support. The
slip is subsequently sintered on the model in a graphite box or
under a protective gas.

The production of metallic dental prostheses for providing   •
15   replacement in the case of dental disease and/or after the loss
of one or several teeth, as for example, inlays, crowns, that can
or cannot be faced with ceramics or plastics, and bridges, is
conventionally carried out by means of the so-called "wax melting
out process", a first quality casting technique assuring a high
20   degree of accuracy to size.

The advantage of the crowns and bridges thus produced must be
seen primarily in the high degree of strength in addition to the
accuracy to size and in the existing ductility, which must be
25   assured for large bridge constructions in order to avoid forced
ruptures in cases of overstrain.

However, the process per se is very time consuming and the
expenditure for material and equipment is high. The necessity of
30   using runners and cast cones requires a markedly increased use of
material as compared with the weight of the vast object, and thus
repeated reuse of this material can result in changes of the
alloying characteristics. In case that this material is not
reused it remains as scrap. A further disadvantage of this
35   process is that in the case of flaws in the cast object repairs
are not possible and the entire production process, starting with

the wax model, must be repeated.

DE-OS 1915977 describes a process for the sinter production of a
metallic dental prosthesis, using a paste consisting of metal
5 powder having a particle size of between 2 and 25 m and a binder
acting as adhesive for moulding the dental prosthesis on a model
of the teeth to be treated. The dental prosthesis is then
sintered. This disadvantage of this process lies in the poor
compressibility of the pastes described since the binder acting
10 as an adhesive cannot be expelled by compression methods, such as
grooving or shaking. Furthermore, since a powder fraction is
used as starting material the density of the green compact is
low. Consequently, the sintering process results in a very
substantial shrinkage and thus in an unacceptable inaccuracy of
15 fit. The use of very fine powders having a particle size of
between 2 and 25 m actually assures a very high degree of
sintering activity but it additionally causes high production
costs.

20 The process for the sinter production of a metallic dental
prosthesis described in US Patent No. 4, 661, 071 uses powders
having a particle size of 5 to 90 m; pasted with a suitable
binder, for moulding the metallic dental prosthesis on a model of
the teeth to be treated. The production of the model requires a
25 castable self-curing stump mass which must be baked at 1400 to
1600°C prior to the application of the metal powder.

Since conventional dental ceramics ovens reach maximal
temperatures of up to approximately 1200°C, a special oven is
30 required. For sintering the metal powder a liquid phase
sintering process is used under a vacuum of 1 to 10^{-2}HPa. Since
conventional dental ceramics ovens cannot reach this vacuum, a
special vacuum oven is required. Furnaces with maximal
temperatures of up to 1400°C and furnaces assuring a good vacuum
35 at high temperatures are much more expensive than standard
ceramics kilns so that the application of these processes

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requires a costly investment for a dental technician.
Furthermore, the use of the liquid phase sintering process also
causes problems with regard to the natural stability during the
sintering process. In order to obtain a compression as fast as
5   possible by rearrangement of the solid component (particles), a
liquid phase proportion of at least 30 to 35% is required (R.M.
German,, Liquid Phase Sintering, Plenum Press, N.Y. Pages 4, 6
and 80). Analogously to the behaviour in dental baking ceramics
chambering and flattening of very delicate details, for example,
10   of an occlusal surface, must be expected and this can cause
problems with regard to the contact points, requiring a
substantial amount of reworking under certain conditions.

DE-OS- 3532331 describes a process for the sinter production of
15   metallic dental prostheses. By using a powder mixture having a
multimodal particle size distribution, which is converted with
water into a mouldable and compressible slip, a controlled high
density of the green compact is thus attained and the degree of
shrinkage during the sintering process remains correspondingly
20   low. This is advantageous for attaining a good accuracy of fit.
The use of water as mixing fluid and of a consistency which is
very similar to that of slips of dental facing ceramics allows an
additional compression by expelling the liquid by means of the
technology used in dental ceramics (grooving or the like). The
25   sintering process can be carried out in a conventional dental
ceramics oven without great expenditure. This can be achieved by
using a graphite box containing the moulded dental prosthesis to
be sintered. This graphite box is put into a conventional oven
for baking dental ceramics and at the sintering temperature the
30   graphite box assures protection against the oxidation of base
metal components of the alloy. However, an adequate reduction of
the partial oxygen pressure can also be attained by injecting a
protective gas into the ceramics baking oven. On completion of
the sintering process the dental prosthesis in the graphite box
35   is cooled in air.

It has been found that that use of powder mixtures of atomized, predominantly spherical noble metal alloys and of precipitated very fine predominantly noble metal powders has disadvantages, namely that with the sintering parameters defined in this process

5   no maximal density values can be attained in the sintered state and that the density of the sintered dental prosthesis decreses distinctly particularly when sintering repeatedly. However, repeated sintering may be necessary when producing bridges in several steps or when making marginal corrections to the edge.

10

Therefore, it is the present invention provides a process for producing a sintered dental prosthesis having a metallic structural matrix of a noble metal or of a noble metal alloy powder mixture with bimodal or multimodal particle size

15   distribution and a predominantly spherical shape, said mixture being stirred with a mixing fluid consisting substantially of water to a slip capable of being moulded and compressible by expelling the mixing fluid, the prosthesis being moulded with said slip on a model of the teeth to be treated, applying the

20   technology used in dental ceramics, said model serving as burner support, said slip subsequently being sintered on the model in a graphite box or under a protective gas, by means of which optimal density values can be attained in the sintered state, particularly when sintering repeatedly, using conventional

25   equipment and technology.

According to the invention the moulded dental prosthesis is first dried in air for 5 to 25 minutes and then subjected to thermal treatment for 5 to 45 minutes at temperatures of between 100 and

30   400°C, whereupon it is heated to 800°C at an average temperature increase of 50 to 300 K per minute and above 800°C it is heated to the sintering temperature T at an average temperature increase of 20 to 200 K per minute in air in the graphite box or under a protective gas, said sintering temperature T lying between

35   $(T_{solidus}-200^{\circ}$C) and $(T_{solidus}-70^{\circ}$C) $T_{solidus}$ being the solidus temperature of the sintered alloy, the sintering process is

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carried out at this temperature for 5 to 45 minutes in the graphite box in air or under a protective gas and thereafter cooling is applied.at temperatures of between $800^{\circ}C$ and room temperature under protective gas or when using a graphite box
5 even under a vacuum of 50 to 1 HPa.

In one embodiment of the present invention the thermal treatment is carried out at temperatures of between 100 and $400^{\circ}C$ for 5 to 25 minutes and the sintering step is carried out for 10 to 30
10 minutes. Suitably the step of heating to the sintering temperature, the sintering and the cooling are carried out under a protective gas under a partial oxygen pressure lower than 5×10^{-2} HPa.

15 Upon drying the moulded and compressed dental prosthesis in air (15 to 25 minutes) it is put, for example, into a graphite box and subjected to thermal treatment in a temperature range of between 100 and $400^{\circ}C$ for 5 to 45 minutes. It is then heated to $800^{\circ}C$ at an average temperature increase of 50 to 300 K per
20 minute and from the preheating temperature to the sintering temperature T in air or under protective gas at 20 to 200 K per minute. The sintering temperature T lies between $(T_{solidus}-200^{\circ}C)$ and $(T_{solidus}-70^{\circ}C)$, $T_{solidus}$ being the solidus temperature of the sintered alloy. The sintering process is
25 carried out at this temperature for 5 to 45 minutes in air or under protective gas, followed by cooling in a temperature range below $900^{\circ}C$ under a vacuum of 1 to 50 HPa or under protective gas. When the cooling process is completed the dental prosthesis can be removed from the graphite box.
30
Heating to the sintering temperature and the sintering process in the graphite box are preferably carried out in air and the cooking process in the temperature range below $900^{\circ}C$ is preferably carried out under vacuum. This is advantageous
35 particularly because of the equipment normally present in a dental laboratory and also with regard to the costs.

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Preferred times for the thermal treatment at temperatures of between 100 and 400°C and for the sintering process are 5 to 25 minutes and 10 to 30 minutes respectively.

5

When the work is not performed in a graphite box, then it must be carried out under protective gas. In the latter case the partiale oxygen pressure should be less than 5×10^{-2} HPa. This is assured, for example, when using industrially pure argon,

10 and++ can be achieved by relatively simple reconstruction of a conventional ceramics kiln.

A special advantage of this process lies in that an adequately high density associated with closed porosity is attained with the

15 above-mentioned parameters, particularly with the vacuum cooling even upon sintering repeatly.

In the process according to the present invention a mixture of predominantly spherical powders having a bimodal or multimodal

20 particle size distribution is used. This powder mixture is mixed with a mixing fluid which substantially consists of water but may also contain small additions of electrolytes, as for example, strontium chloride, copper chloride or ammonium nitrate, monohydric or polyhydric alcohols, celluslose or polyethylene

25 glycol, either by hand or with a stirrer suitable for this purpose so as to obtain a slip whose consistency and moulding properties correspond to those of conventional dental and facing ceramics.

30 The slip thus prepared is coated on a high temperature-resistant model of the teeth to be treated, applying the technology commonly used in dental ceramics. On said model the slip is compressed by means of conventional methods (for example, shaking with the grooved portion of a moulding instrument, ultrasound,

35 etc). The fluid thus gets to the surface, which is cleaned off with a cloth or dried in a warm air stream. It is advisable to

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impregnate or insulate the stump with a liquid prior to the application of the slip so that the moisture is not removed from the slip by the stump.

5   The green compact compressed to a high gross density is allowed to stand on the model in air for approximately 5 to 25 minutes in order to dry slowly. This can also clone on the top plate of a ceramics baking kiln that normally has temperature of $\leq 50^{\circ}C$. The dental prosthesis on the model is then put into a graphite

10   box which completely encompasses the model.

The dental prosthesis is then subjected to a thermal treatment in an oven for 5 to 45 minutes at a temperature of between 100 and $400^{\circ}C$. The aim of this thermal treatment is the removal of

15   moisture possibly still present or of organic impurities. If this thermal treatment is not carried out prior to the actual sintering process, this will result in the formation of cracks in the walls of the crown. When the temperature of $400^{\circ}C$ are exceeded and the temperature is maintained corresponding to the

20   defined times, then the density of the sintered dental prosthesis will drop drastically.

On completion of the thermal treatment the graphite box with the dental prosthesis therein is heated to the sintering temperature.

25   In order to attain a sufficiently high sintering density, it is necessary to bridge the temperature range of between $400^{\circ}C$ and $800^{\circ}C$ with an average heating rate exceeding 50 K per minute, particularly a rate of 50 to 300 K per minute.

30   Lower heating rates result in a reduced density. At temperatures above $800^{\circ}C$ it is favourable to select an average heating rate of between 20 and 200 K per minute. This results in acceptable times also with regard to the total sintering time.

35   The density of the sintered dental prosthesis depends on the sintering temperature T. Surprisingly it has been found that the

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density has a maximum in the temperature range of between $(T_{solidus}-200^\circ C)$ and $(T_{solidus}-70^\circ C)$, the exact position depending in turn on the specific alloy. The maximum extends over a temperature range of 20 to $50^\circ C$ and a very substantial
5 drop of the density values is observed on exceeding this maximum. Two typical curves for two powder mixtures are shown in the drawing.

The dental prosthesis in the graphite box can be sintered in air
10 or under protective gas. The sintering process is preferably carried out in air since the results obtained are not poor than those obtained under protective gas and since the expenditure for equipment is comparatively lower.

15 The sintering time isi 5 to 45 minutes and as a rule the maximal density is attained at sintering times of as low as between 10 and 30 minutes.

Cooling the sintered dental prosthesis in the graphite box in air
20 does not result in high densities after the first sintering step. However, for the production of bridges or for the correction of the occlusion, the contact points or of the edge end a second sintering step is required. Despite the identical sintering cycle the density of the sintered dental prosthesis decreases
25 drastically upon sintering twice. Surprisingly it has now been found that by cooling the dental prosthesis in the graphite box under a vacuum of between 50 and 1 HPa the density drop upon sintering repeatedly can be prevented. However, it is crucial that the required vacuum is present before the dental prosthesis
30 is cooled to a temperature < $900^\circ C$.

The sintering process can also be carried out without a graphite box but in that case it must be carried out under protective gas and the above-mentioned data on temperature and time also apply.
35 The partial oxygen pressure in the protective gas must not exceed 5×10^{-2} HPa in order to attain a sufficiently high density. The

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cooling process must then also be carried out under protective gas.

The following Examples will illustrate the process according to
5   the present invention:

Example 1
By adding a mixing fluid of 98% of H_2O and 2% of polyethylene glycol to the slip from the powder mixture 1 (Table 2) a
10   consistency suitable for moulding was imparted to the slip. With the aid of a brush the slip is coated on a stump impregnated with a liquid. The crown is completely moulded and the slufe is checked again and again in the articulator.

15   The slip is compressed by grooving with a moulding instrument. The fluid emerging from the surface is removed with a cloth. The good stability of the slip allows the construction of details of the occlusal surface such as humps or troughs. After the compression (water no longer emerges from the surface) the
20   surface can be reworked by scraping or carving so that fine fissures can also created prior to the sintering process. The completely moulded crown remains on the stump during the entire sintering process and is then placed on the cover plate of a ceramics oven in order to dry it. After 15 minutes it is put
25   into a graphite box comprising a graphite bottom with a corresponding receptacle for the stump and a cup-shaped graphite cap. The graphite box with the moulded crown is put into an oven which is simultaneously heated to 300°C. After 15 minutes the graphite box is put into a ceramics baking kiln preheated to
30   1000°C. The temperature is increased to 1050°C. The sintering temperature of 1050°C is reached after 5 minutes corresponding to an average heating rate of 150 K per minute. The sintering temperature of 1050°C is 160°C below the $T_{solidus}$ temperature of 1210°C (see Table 2). After 20 minutes the graphite box is
35   removed from the kiln and cooled in air. A number of small corrections are required on the occlusal surface and in an edge

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region. The points to be corrected are subsequently marked on
the sintered crown in the above described manner. The crown is
then sintered once more, using the above-described sintering
cycle. On checking the density a value of 14.2 g/cc is obtained.
5 . The crown is too large because it was cooled in air.

Example 2
A further crown is produced analogously to Example 1. However,
on completion of the sintering process at 1050°C the crown is
10 transferred into a cooling chamber that can be evacuated.
Immediately upon transferring the graphite box the cooling
chamber is evacuated to a vacuum of approximately 50 HPa. After
approximately 15 minutes the cooled specimen can be removed. As
described in Example 1 a number of small corrections are made.
15 The crown is sintered once more and again cooled under vacuum.
The stump mass is blasted, using a sand blast apparatus and the
density is determined. It now is 16.1 g/cc; the porosity is
closed. The crown is perfected and polished. The edge fissure
on the master model is on the average 40 m.
20

Example 3
For the production of inlays the powder mixture 2 (Table 2) is
used since this alloy is yellow and is preferred by many
patients. Furthermore, this alloy has a lower 0.2% offset yield
25 strength and an increased ductility. This allows the edges to be
more easily worked with pieces in the mouth. The production is
carried out analogously to that of the process described in
Example 2.

30 However, the sintering cycle is slightly modified. After being
dried in air the inlay on the model stump (in the graphite box)
is placed on the baking table of an open ceramics baking oven
that has been preheated to 700°C,. The temperature on the baking
table is approximately 250°C. After 9 minutes the baking table
35 runs in automatically into the oven which heats up to the
sintering temperature of 940°C. After further 15 minutes the

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specimen can be removed from the oven and transferred to the
cooling chamber, where it is cooled under a vacuum of 50 HPa.
The stump mass is blasted, the inlay is perfected, put on the
master model stump and polished. The density is 17.1 g per ce

5   and the porosity is closed. The pores located on the surface are
closed by the polish. The edge fissure is approximately 50 m.
The rate of change of temperature between 400 and 800°C is on the
average approximately 120 K per minute. The rate of change of
temperature between 800°C and the sintering temperature is on the

10   average 100 K per minute. $T_{solidus}$ is 1040°C (Table 2)

Palladium alloys can also be processed in the same manner.

The composition of the alloys used in the examples, their

15   production, particle shape and particle size have been compiled
in Table 1. The compositions of the powder mixtures used in the
examples have been compiled in Table 2

The sintering density of the dental prosthesis parts according to

20   the powder mixtures of Table 2 is shown in the drawing as a
function of the sintering temperature.

TABLE 1

Examples of Powders Used

	Compos-ition (mass pro-portion in %)	Particle Shape	Production	Particle Size/ m
Alloy 1	Au 65 Pt 15 Pd 13, In 2.5 + additives each <2%	predominantly spherical	atomization	-*
Alloy 2	Au 87 Pt 11 + additives each <2%	predominantly spherical	atomization	-*
Au Powder 1	Au	predominantly spherical	chemical precipita-tion	<5r
Au Powder 2	Au	predominantly spherical	chemical precipita-tion	<10.

* depending on screening, always < 100 m

TABLE 2

	Component 1 powder content KG**/ m %	Component 2 powder content KG/ m %	Component 3 powder content KG/ m %	$T_{solidus}$*
Powder Mixture 1	alloy 1 80 < 63	Au 1 20 < 5		1210°C
Powder Mixture 2	alloy 2 85 < 50	Au 1 13 < 5	Au 2 2 < 10	1040°C

* $T_{solidus}$ of the sintered alloy

** KG = particle size

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for producing a sintered dental
prosthesis having a metallic structural matrix of a noble metal
or of a noble metal alloy powder mixture with bimodal or
multimodal particle size distribution and a predominantly
spherical shape, said mixture being stirred with a mixing fluid
consisting substantially of water to a slip capable of being
moulded and compressible by expelling the mixing fluid, the
prosthesis being moulded with said slip on a model of the teeth
to be treated, applying the technology used in dental ceramics,
said model serving as burner support, said slip subsequently
being sintered on the model in a graphite box or under a
protective gas, in which the moulded dental prosthesis is first
dried in air for 5 to 25 minutes and then subjected to thermal
treatment for 5 to 45 minutes at temperatures of between 100 and
$400^{o}C$, whereupon it is heated to $800^{o}C$ at an average temperature
increase of 50 to 300 K per minute and above $800^{o}C$ it is heated
to the sintering temperature T at an average temperature increase
of 20 to 200 K per minute in air in the graphite box or under a
protective gas, said sintering temperature T lying between
($T_{solidus}- 200^{o}C$) and ($T_{solidus}-70^{o}C$). $T_{solidus}$ being the
solidus temperature of the sintered alloy, the sintering process
is carried out at this temperature for 5 to 45 minutes in the
graphite box in air or under a protective gas and thereafter
cooling is applied at temperatures of between $800^{o}C$ and room
temperature under a protective gas or when using a graphite box
even under a vacuum of 50 to 1 HPa.

2. A process according as claimed in claim 1, wherein
the thermal treatment is carried out at temperatures of between
100 and $400^{o}C$ for 5 to 25 minutes and the sintering step is
carried out for 10 to 30 minutes.

3. A process as claimed in claim 1 or 2, wherein the step of heating to the sintering temperature, the sintering and the cooling are carried out under a protective gas under a partial oxygen pressure lower than 5×10^{-2} HPa.

4. A process as claimed in claim 1 or 2 in which the heating to the sintering temperature and the sintering of the graphite box are carried out in air and the cooling in the temperature range below $900^{\circ}C$ is carried out under vacuum.

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Powder mixture 1
Powder mixture 2
Drying temperature 300°C (Table 2)
Graphite box
Air
Sintering time 15 min.